Aqua Ammonia Process for Simultaneous Removal of CO_2, SO_2, and NO_x

Kevin P. Resnik[1], James T. Yeh[2], and Henry W. Pennline[2]

[1] Parson Project Services, Inc., P.O. Box 10940, Pittsburgh, PA, USA, 15236

[2] U. S. Department of Energy, National Energy Technology Laboratory, P.O. Box 10940, Pittsburgh, PA, USA, 15236

BIOGRAPHY:

K.P. Resnik is a process engineer with Parson Project Services, Inc., the site-support contractor for the in-house operations at the U. S. Department of Energy's National Energy Technology Laboratory. He has worked with air pollution abatement systems over the past 15 years. J.T. Yeh is a project leader with the DOE and has been involved in environmental projects in the past. H.W. Pennline is a team leader in the carbon dioxide capture area responsible for various projects in the sequestration area.

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ABSTRACT

Experimental research work in applying aqueous ammonia solution for the simultaneous reduction of acidic gaseous emission from fossil fuel-fired utility plants is currently being performed at the National Energy Technology Laboratory. The traditional monoethanolamine process for CO_2 removal suffers the disadvantages of low carbon dioxide loading capacity, equipment corrosion, amine degradation by SO_2 and O_2 in flue gas, and high energy penalty during absorbent regeneration. The aqueous ammonia process can simultaneously remove CO_2, SO_2, NO_x, plus HCl and HF that may exist in the flue gas. SO_2 and NO could be oxidized prior to contacting the aqueous ammonia absorbent. Test results pertaining to the ammonia/carbon dioxide reaction in a semi-continuous reactor system are presented. The parametric effects of sparger design, reaction temperature, and ammonia concentration on gas loadings and absorption rates are discussed. Regeneration test results, including solution cycling between the regeneration and absorption steps to determine a realistic loading capacity for the ammonia solutions are also presented.

INTRODUCTION

There is a serious concern that large amounts of carbon dioxide (CO_2) being emitted into the atmosphere through human activities, mainly through the burning of fossil fuels, could cause global climate changes. Therefore, the CO_2 concentration level in the atmosphere should be stabilized or reduced to a level that the world community can agree upon. The cost to capture CO_2 from power generation point sources using current technology is very high. It is estimated that the energy penalty from using the well known monoethanolamine (MEA) process for CO_2 capture from coal-fired power plants is about 35% [1], but can be lowered to about 15% in a best case scenario [2]. While these MEA-based technologies are commercially viable to produce CO_2 for the food processing and chemical manufacturing industries, they are considered to be too costly for the removal of CO_2 from power plant flue gases for potential sequestration purposes. Recently, a number of energy efficient proprietary solvents have been developed that are based on either sterically hindered amines or formulated amines. These amines could save regeneration costs by up to 40%; the separation cost per ton of CO_2 ranges from 40 to 70 US dollars [3]. However, an economic tradeoff in capital costs would likely occur, since the slower reacting amines will require a larger absorber (longer gas-liquid contact time) to achieve the same CO_2 capture as compared to MEA

The MEA process suffers the following disadvantages for CO_2 separation from flue gases: (1) low carbon dioxide loading capacity (kg CO_2 absorbed per kg absorbent); (2) high equipment corrosion rate; (3) amine degradation by SO_2, NO_2, HCl and HF, and oxygen in flue gas which induces a high absorbent makeup rate; and (4) high energy consumption during high temperature absorbent regeneration. When capturing CO_2 from coal or petroleum-derived combustion flue gas, the MEA process requires that SO_2 be removed first from the flue gas stream, since MEA is degraded by SO_2 and oxygen, forming irreversible degradation products. The annual cost of MEA makeup is high

because of degradation, even after most of the SO_2 is removed from the flue gas in an upstream flue gas desulfurization process. NO_x must also be eventually removed from the flue gas before it is discharged into the air in order to meet present and future gaseous emission limits. NO_x removal would occur upstream of the CO_2 absorber. Low NO_x burners and/or selective catalytic reduction would be required to reduce the NO_x level.

It is envisioned that the current widely utilized MEA Process could be replaced with a single Aqua Ammonia Process to capture all three major acid gases (SO_2, NO_X, CO_2) plus HCl and HF, which may exist in the flue gas. Since SO_2 and NO_X emissions must comply to certain emission limits, a single process to capture all acidic gases is expected to reduce the total cost and complexity of emission control systems. Currently there is no emission limit on CO_2, although a limit on CO_2 emission in the future may become a reality. Unlike the MEA Process, the Aqua Ammonia Process does not have absorbent degradation problems that are caused by sulfur dioxide and oxygen in flue gas and does not cause equipment corrosion, as in the case of MEA. Other economic reasons in considering the ammonia process exist.

The major byproducts from the Aqua Ammonia Process include ammonium sulfate, ammonium nitrate, and ammonium bicarbonate. Ammonium sulfate and ammonium nitrate are well known fertilizers for certain crops. Ammonium bicarbonate has been utilized by certain developing countries as a crop fertilizer for over 30 years with proven results in farmland practice which enhanced crop root development and leaf growth [4]. Ammonium bicarbonate was rated by Kirk-Othmer [5] as having definite fertilizing value but can not compete with other ammonium compounds, for example, ammonium sulfate or urea. China produces a so called Modified Ammonium Bicarbonate (MAB), which is a stabilized, less volatile, form of ammonium bicarbonate produced by the addition of a patented additive (Chinese patent: ZL90105012). Ammonium bicarbonate also has other industrial usages. For instance, the baking industry uses the powder to produce gases in baked goods without leaving any solids behind. Another example is for removal of calcium sulfate scales on heat exchanger tubes. More usages can be found in the Encyclopedia of Chemical Technology.

As an alternative to using ammonium bicarbonate byproduct as fertilizer, the ammonia (NH_3) content in ammonium bicarbonate could be regenerated for recycle. Ammonium bicarbonate decomposes at a relatively low temperature of 60^oC [6]. This compares with a 120^oC regeneration temperature for MEA solutions. Ammonia gas and carbon dioxide gas can be separated by using ammonia's high solubility-in-water property. Carbon dioxide in pure form will subsequently be separated.

To facilitate the control of multipollutants, the proposed control process would pretreat the flue gas by oxidizing sulfur dioxide (SO_2) and nitric oxide (NO) to SO_3 and NO_2, respectively, in an oxidization step before treating the flue gas with aqueous ammonia in a wet scrubber. NO_x nominally consists of approximately 97% NO and 3% NO_2, but only NO_2 can dissolve readily in an ammonia solution to form NH_4NO_3. SO_2 is oxidized to SO_3 during the oxidation step and will form ammonium sulfate when reacted with ammonium hydroxide. SO_2 was not oxidatively treated in General Electric's Ammonium Sulfate Process, currently Marsulex Ammonium Sulfate Flue Gas

Desulfurization technology [7,8,9]. Rather, SO_2 reacts with ammonium hydroxide to form ammonium sulfite, followed by forced air to oxidize sulfite to sulfate. Ammonium sulfate is less volatile than ammonium sulfite, making ammonium sulfate a less volatile fertilizer. Furthermore, the aqueous ammonia process can remove any HCl and HF from the flue gas.

The Ammonium Sulfate Process does not reduce NO, which constitutes a vast majority of the NO_x. There is a commercial process currently in operation, which utilizes ammonia for removal of SO_2 and NO_x in flue gas, in a hybrid wet and dry mode [10]. This AMASOX and NO_x removal technology is operated by Krupp Koppers GmbH in Germany. It is not a simultaneous removal process, rather, SO_2 is first removed in a wet scrubber using aqueous ammonia as the absorbent, which is similar to the Marsulex technology. The Koppers process goes a step further and after SO_2 removal, the flue gas is reheated to at least 300 ^{o}C and NO_x is reduced in a SCR reactor using ammonia gas for NO_x destruction. The saleable byproduct is ammonium sulfate in slurry form, which can be used directly as a fertilizer or can be reprocessed into crystal form if longer distance transportation is required to sell the byproduct. Neither Marsulex [8] nor Koppers [10] discusses the subject of CO_2 capture by ammonia solution. Only enough ammonia solution is sprayed to stoichiometrically react with SO_2 in the flue gas, and thus any minute change in CO_2 concentration in flue gas was not noticeable. It should be noted that SO_2 concentration in flue gas is only a small fraction of the CO_2 concentration, and the ammonia solution reacts preferentially with SO_2. Walsh's report [8] discussed Dakota Gasification Plant's Ammonium Sulfate Process in some detail. Again, the fate of CO_2 in flue gas was never discussed. Marsulex sells ammonium sulfate fertilizer, and for every ton of ammonia, 4 tons of fertilizer is produced. Marsulex's process increases the value of ammonia from 70% to 400%, depending upon the location of the plant producing it and normal market fluctuations.

Currently, there is only one known commercial process that uses ammonia to simultaneously remove SO_2 and NO_x from flue gas within one reactor and produce mixed ammonium sulfate and nitrate fertilizer [9]. This Ebara E-Beam process, with one plant in operation in China, uses a high energy flux of electrons to irradiate the flue gas stream in an effort to oxidize SO_2 and NO_x. Ammonia is injected into the flue gas and reacts with the acid precursors to form ammonium sulfate and ammonium nitrate particulates. The particulates are collected downstream in an electrostatic precipitator or fabric filter and transferred to a storage silo. The higher the applied electron beam power the more efficient the SO_2 and NO_x removal. In other words, it is a tunable process, but it could be with a steep energy penalty. High energy beam or irradiation techniques, in general, are not the only method to oxidize SO_2 and NO_x.

Gas-phase oxidation of nitric oxide to NO_2 can be accomplished by strong oxidizers. One oxidation procedure is carried out by injecting liquid hydrogen peroxide into the flue gas; the H_2O_2 vaporizes and dissociates into active hydroxyl radicals which oxidize the NO to NO_2 [11]. Hydrogen peroxide as an oxidant can also be effective in aqueous solutions [12]. Nitric oxide can also be oxidized at low to moderate temperature using ozone [11, 13, 14]. Ozone may be replaced by chlorine dioxide to oxidize NO [13].

Very few research reports in the usage of ammonia for CO_2 capture exist, but the most noted ones

are from Bai and Yeh [15] and Yeh and Bai [16]. Bai's 1997 publication reported obtaining crystalline solids of NH_4HCO_3 by sparging CO_2 into ammonium hydroxide solution, and in the 1999 publication, data were published comparing maximum CO_2 loading capacity in MEA solution and in ammonium hydroxide solution on equal weight-of-absorbent basis. It was concluded that the maximum CO_2 removal efficiency by NH_3 absorbent can reach 99% and the CO_2 loading capacity can approach 1.20 kg CO_2/kg NH_3. On the other hand, the maximum CO_2 removal efficiency and loading capacity by MEA absorbent are 94% and 0.40 kg CO_2/kg MEA, respectively, under the same test conditions. In other words, ammonia's CO_2 loading is 3 times that of MEA's. Yeh et al. [16] plotted liquid absorbent temperature versus time during the CO_2 absorption experiment and observed that the heat of reaction with MEA was greater than with ammonia. They also found that the purchase price for industrial grade NH_3 solution is approximately one-sixth of that of the MEA absorbent on the same weight basis in the world market. NETL's own preliminary research in aqueous ammonia scrubbing of CO_2 in a packed bed absorber produced similar CO_2 removal results [17] as compared to Yeh et al. [16].

In view of the shortcomings of the MEA process for CO_2 capture, Wolsky et al. [18] suggested that future research efforts should be directed toward developing better solvents for removal of CO_2. An ideal absorbent should have a CO_2 loading capacity of at least 1.0 kg of CO_2 per kg of solution and that the regeneration energy requirement must be much lower than the MEA process.

The Aqua Ammonia Process seems to have avoided the shortcomings of the MEA process. In consideration, the following apply: (1) aqueous ammonia has high loading capacity; (2) aqueous ammonia does not pose a corrosion problem; (3) there is no absorbent degradation problem, thus reducing absorbent makeup rate; and (4) the energy requirement for absorbent regeneration is predicted to be much lower than in the MEA process. Prior to this study, it has been estimated that thermal energy consumption for CO_2 regeneration using the Aqua Ammonia Process could be at least 75% less than if the MEA Process is used for CO_2 absorption and regeneration. Above all, the saleable, income-producing byproducts, ammonium sulfate and ammonium nitrate as fertilizer alone, will promote the burning of cheap and abundant high-sulfur coals. Higher sulfur content coals will generate higher income for the power plants and lower the cost of power generation. At this point, it is uncertain if there is market for ammonium bicarbonate fertilizer. Therefore, it is assumed that ammonium bicarbonate will be decomposed and ammonia will be recycled to the CO_2 capture system where carbon dioxide will be recovered and eventually sequestered.

EXPERIMENTAL
The CO_2 absorption rate studies were performed in a semi-continuous flow reactor as shown in Figure 1. The simulated flue gas consists of 15%vol CO_2 and 85%vol N_2. The gases were supplied by compressed gas cylinders and the flow controlled by mass flow controllers. The CO_2 absorber was a 3-liter glass container filled with 1500-ml aqueous ammonia solution. Pressure was near atmospheric; total gas flowrate was 7500 sccm. The temperature of the absorber was controlled with a cooling/heating coil, through which temperature-controlled water flowed. The baseline condition for the tests was 80°F. The simulated flue gas entered the absorber through one of two cylindrical-shaped sintered metal spargers for most of the parametric studies. The sparger was made of sintered stainless steel (2 micron pore). The dual sintered metal spargers were installed after several failed

test runs, that were caused by plugging of the sparger due to ammonium bicarbonate crystal formation.

The vent gas from the absorber was sent through a coil, which was immersed in an ice bath, reducing the gas temperature to 35^0F to condense the vapor escaping from the absorber. The condensed vapor and carried-over mist from the absorber was drained periodically. The vent gas volumetric flowrate was measured by a bagmeter. The gas from the bagmeter was then analyzed for unreacted CO_2 gas before being vented. An Horiba Model VIA-510 CO_2 Analyzer gave continuous readings. The CO_2 concentration-versus-time data were used to calculate CO_2 absorption rates and to totalize the amount of CO_2 absorbed. Data was recorded every ten seconds for the duration of a test. The baseline condition for the tests was 80^oF, utilizing a 14% ammonia solution.

After the first series of tests that were used to gather rudimentary kinetic information, several improvements were made to the system. The vent line volumetric flow meter was replaced by a mass flow meter to allow continuous vent flow measurements. The ice bath was replaced with a reflux condenser, reducing the gas temperature to 10^oF, assuring that negligible water vapor was present in the vent line. The spargers were replaced with an open tube and a mechanical mixer with a 6-blade Rushton-type turbine impeller operating at 1400 rpm was installed. The impeller speed at which gross recirculation of gas into the liquid occurs was calculated to be 748 rpm, using a correlation of Lee and Tsui [19]. Provisions were made to take liquid samples during the test for chemical analysis. In the data reduction scheme, it was assumed that the major constituents from the regeneration tests were N_2, CO_2, and NH_3. The N_2 flow was measured by the inlet mass flow controller. The total flow from the reactor was measured by the outlet flow meter. The CO_2 flow was calculated based on the total flow and the CO_2 concentration. The NH_3 flow was calculated by difference. The modified system was used to determine the effect of cycling the solution between the absorption and regeneration steps.

Regeneration of the solution was performed using a majority of the equipment described above, with the following exceptions. A 2-liter reactor was used to minimize the reactor headspace. The nitrogen gas flow was reduced to approximately 1000 sccm and was utilized only as a sweep gas to reduce the residence time to the CO_2 IR analyzer (i.e., the nitrogen did not flow through the reactor, but was connected to the vent line). The solution was heated using the cooling/heating coil. The solution temperature was ramped from 120^oF to as high as 190^oF, with liquid samples taken at each step. The CO_2 regenerated and the NH_3 evaporated were totalized with data taken every ten seconds. The regeneration was investigated for solutions containing various mixtures of ammonium bicarbonate and of ammonium carbonate in water or spent ammonia solutions which had undergone an absorption step.

Solutions of 7%, 10.5%, and 14% ammonia were used in cycling tests to determine the potential effective utilization rates available for the aqueous ammonia solutions. As before, ammonia solutions were made by mixing A.C.S grade ammonium hydroxide solutions with water to provide the desried concentrations. For the cycling tests, the mixer with open tubing was utilized at 80^oF. After the initial absorption test, the resultant solutions were thermally regenerated to 180^oF. The absorption/regeneration cycle was repeated for a total of three cycles, anticipating that the amount of

CO_2 absorbed in the absorption step and regenerated in the regeneration step would equilibrate by the third cycle.

DISCUSSION OF RESULTS

The CO_2 absorption rate by aqueous ammonia solution was calculated by CO_2 breakthrough concentration versus time. Experiments were run at 60°F, 80°F, and 100°F, respectively. Five sparger designs were initially tested for their effects on CO_2 absorption rates with the aqueous ammonia solution. Regeneration tests were performed on standard solutions. Additionally, cycling tests were conducted.

Effect of Sparger Types

The effect of sparger types was initially conducted using 14% ammonia solution at 80°F absorber temperature. During the test, 7500 sccm of simulated flue gas (15% CO_2, 85% N_2) bubbled through the sparger and into 1.5 liter of absorbent. CO_2 concentration from the vent was continuously monitored for absorption rate calculations. Five sparger types/designs were tested and are discussed below.

Sintered metal, flat panel with 1-micron pores

The sintered stainless steel sparger of 3-7/8-in diameter was lowered into the reactor at approximately 1 inch above the bottom of the glass reactor (5-in diameter). The CO_2-laden stream flowed into the solution through the sparger while the breakthrough concentration of CO_2 was measured continuously with the CO_2 analyzer. This sparger provided excellent gas distribution in the reactor. The gas bubbles broke up into a cloud-like foaming layer within the top half of the solution in the reactor. It was expected that at the end of CO_2 breakthrough curve, the CO_2 concentration should reach 15%, which is the CO_2 inlet concentration to the reactor. However, at about 7% CO_2 concentration, the sparger pressure drop increased and the gas flow was shut off by a pressure drop protective device. After encountering additional failed tests, it was determined that the blockage must be caused by the formation of crystalline ammonium bicarbonate; wet seed crystals lodged in the sintered metal pores. White powder was observed after the glass reactor was dried. Bai and Yeh [15] observed white powder in their experimental apparatus (implying a dry condition). During testing, if the gas flow was stopped for a short time (10 minutes or so), the extent of the blockage would decrease.

Cylindrical shaped sintered metal with 2-micron pores

The flat panel sintered metal was replaced with a cylindrical-shaped sparger (3/8-in dia and 2 3/4-in active length) with 2 micron pores. It also experienced similar blockage problems as the flat sintered metal sparger.

Tubing with 1/64-in diameter holes or with 1/16-in holes

Since the invisible crystal seeds can easily plug up the sintered metal micron-sized pores, a simple holes-in-tubing sparger was installed in the reactor. Nonetheless, pluggage still occurred, but at a much delayed pace, even for the larger diameter holes. Thirty holes were drilled in each 2 1/4-in

long and 3/8-in diameter piece of tubing. This simpler sparger allowed the breakthrough CO_2 concentration to reach 14%, only 1% below the reactor inlet CO_2 concentration. Although this was a huge improvement over the sintered metal sparger, a much slower CO_2 absorption rate into the absorbent occurred, due to the much larger bubble size causing poor gas-liquid contact. Poor gas-liquid contact resulted in more unreacted CO_2 escaping through the vent line.

Dual-sparger design
To take advantage of the apparent re-dissolving of the crystals with no gas flow, a design connecting two of the cylindrical sintered metal spargers (see above) with a common feed line was used. The gas enters the reactor through one of the cylindrical spargers. When pressure builds up, the one sparger is isolated while the gas flow is switched to the other. It was speculated that the crystals lodged in the pores re-dissolve into the solution if CO_2 gas is stopped for a short time.

Mixer with Open Tubing
To further reduce the possibility of plugging the reactor, the system was modified to allow for a mechanical mixer to be installed through the reactor head. The mixer powered a six bladed, high shear radial impeller. Four baffles extended the length of the reactor at a 90-degree angle from the wall. The gas was introduced with stainless steel tubing (3/8 in) that was bent such that the gas was introduced in the center of the reactor flowing vertically. The impeller, operating at 1400 rpm, was located 0.25 in above the tubing outlet. It should be noted that although progress was made toward the goal of CO_2 breakthrough, formation of the precipitate was still significant enough to plug the open end of the tubing after approximately 5 g-moles of CO_2 were absorbed in the solution.

Figure 2 shows the effect of the types of spargers. The two lowest curves show the slowest CO_2 absorption rates. The tubing with the 1/16-in diameter holes exhibits the lowest CO_2 absorption rate, followed by the tubing with 1/64-in diameter holes. The sintered metal spargers and the open tube utilizing the mixer all had essentially equivalent absorption rates as a function of the amount of CO_2 absorbed. For these tests, the CO_2 absorption rates of all three sintered spargers and the open tube with the mixer have nearly merged. The implication is that in these systems, the reaction kinetics dominates the reaction; the gas-liquid contact is of secondary importance. This along with gas pressure drop is important with respect to reactor optimization and economic considerations.

Figure 3 shows the raw data used to produce Figure 2. It is a plot of CO_2 concentration in the vent gas versus time elapsed since the experiment began. The sintered-metal spargers and the open tube utilizing the mixer offer the higher rate of CO_2 depletion. The top curve (sparger with larger holes) exhibits the slowest rate of CO_2 removal or the highest concentration of unreacted CO_2 breakthrough. The reaction was able to proceed further for the sparger with holes for two reasons: the larger holes were more difficult to plug, and the slower reaction rates provided time for the ammonia in the solution to evaporate, lowering the potential ammonium salt concentration. The lower salt concentration is also evidenced by the fact that the total amount of CO_2 absorbed (Figure 2) is less for the tubing with holes.

Effect of NH$_3$ Concentration in Solution on Absorption Rate
The effects of ammonia concentration on CO_2 absorption rate are illustrated in Figures 4, 5, and 6.

Although the initial absorption rates are similar, as the CO_2 absorption reaction progresses, the rates are higher for solutions with the higher ammonia concentrations. As expected, CO_2 took a longer time to breakthrough the solutions having higher ammonia concentration. For overall absorptivity of CO_2, the data patterns indicate that it is more advantageous to use a higher concentration ammonia solution as CO_2 absorbent. The conclusions are the same at all three reaction temperatures. All the tests were run with the dual cylindrical sparger design as discussed in the previous section. The sudden rise of reaction rates coincided with switching from the plugged cylinder to the clean cylinder. The clean cylinder allowed normal CO_2 flow to enter the reactor without the hindrance by the seed crystals of NH_4HCO_3 product.

Effect of Reaction Temperature on Absorption Rate
Three reaction temperatures (60^oF, 80^oF, and 100^oF) were tested at ammonia solution concentrations of 7%, 14%, and 21%. The results are also shown in Figures 4, 5, and 6. Dual cylindrical spargers were used in all tests. Because the decomposition temperature of NH_4HCO_3 is near 140^oF, reactor temperatures above 100^oF were not considered. The net amount of CO_2 absorbed decreases with increasing temperature, and it may be favorable to operate the reactor at the low temperatures. Yeh and Bai [16] reported that CO_2 absorption capacity of ammonia solution (28% concentration) decreased by 11% between reaction temperatures 50^oF and 104^oF. As the temperature approached the ammonium carbonate/bicarbonate decomposition temperature, the CO_2 absorption rate decrease is expected. The concentration and temperature effects are important considerations when determining the reaction kinetics.

Regeneration of Ammonium Bicarbonate and Ammonium Carbonate
Figure 7 shows the amount of carbon dioxide liberated by thermal regeneration from standard solutions of ammonium bicarbonate (ABC) and ammonium carbonate (AC) as a function of temperature. The dependent variable in Figure 7 represents the total percentage of the original carbon in the solution that was evolved up to that temperature. It is evident that as the proportion of bicarbonate in the solution increases, the carbon dioxide is more easily regenerated. It is demonstrated that as much as 60% of the carbon in the solutions can be regenerated, which in a continuous process would free the ammonia for the absorption cycle.
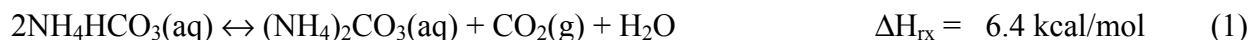
Cycling Tests of Aqueous Ammonia Solutions
Figures 8, 9, and 10 show the CO_2 absorption rate per gram of solution as a function of time for three cycles at 7%, 10.5%, and 14% aqueous ammonia solutions, respectively. The regeneration step heated the solution to 180^oF. These graphs indicate that there is a dramatic change in the absorption capacity between the first and second cycles, but little change thereafter. These results indicate that less than 100% regeneration of the initial solution is achieved, and that significant evaporation of the ammonia is evident. Of the initial 198 g of ammonia in the 14% solutions, 85.4g (43%) was lost in the vent lines during the cycling tests, with 71.5 g being lost in the first absorption step. For the 10.5% and 7% solutions, 32% and 30% of the ammonia were vented, respectively, with similar proportions of ammonia being released during the first absorption step. A large amount of ammonia is lost when a fresh ammonia solution is used for CO_2 capture in the impeller driven semi-continuous reactor. After the CO_2-rich ammonia solution is regenerated by heating, the solution is a CO_2-lean ammonia solution and it can be

reused to capture CO_2. The high loss of ammonia during the first absorption cycle is called the initial condition effect. There is very little additional ammonia lost during the second absorption and third absorption, as in a continuous process, where the ammonia vapor pressure would be much lower, because ammonia is being tied up with CO_2 to form ammonium carbonate and ammonium bicarbonate. The initial condition effect would be suppressed in a continuous process. Fresh ammonia solution would only be fed as a makeup solution. Therefore little free ammonia is present in the flow stream at any moment resulting in low NH_3 vapor pressure.

Figure 11 displays the specific absorption capacity of the solutions for each cycle, also demonstrating that the experiments appear to have reached equilibrium after the second absorption test. The results with aqueous ammonia are far from optimized with respect to the amount of CO_2 regenerated and the amount of ammonia lost. The final measured specific absorption capacity is 0.068 g CO_2/g solution, 0.053 g CO_2/g solution, and 0.040 g CO_2/g solution for the 14%, 10.5%, and 7% ammonia solutions, respectively. This compares favorably to current MEA technology that has demonstrated a capacity of 0.036 g CO2/g solution for a standard 20% MEA solution [20]. The sensible heat of regeneration per mass of CO_2 is indirectly proportional to the loading and proportional to the temperature difference between the absorption and regeneration temperatures (131^oF to 248^oF for MEA, 80^oF to 180^oF for aqueous ammonia). Using the above absorption capacity data, the sensible heat of regeneration for the aqueous ammonia process may be as little as 45% that of the MEA process.

Three potential reactions could be responsible for liberation of CO_2 during the thermal regeneration.

$2NH_4HCO_3(aq) \leftrightarrow (NH_4)_2CO_3(aq) + CO_2(g) + H_2O$ $\quad\quad$ $\Delta H_{rx} = $ 6.4 kcal/mol $\quad$ (1)
$NH_4HCO_3(aq) \leftrightarrow NH_3(aq) + H_2O + CO_2(g)$ $\quad\quad\quad\quad$ $\Delta H_{rx} = $ 15.3 kcal/mol $\quad$ (2)
$(NH_4)_2CO_3(aq) \leftrightarrow 2NH_3(aq) + H_2O + CO_2(g)$ $\quad\quad\quad$ $\Delta H_{rx} = $ 24.1kcal/mol $\quad$ (3)

The heat of reaction for the MEA process has been reported to be 20.0 kcal/mol [7]. Regardless of the reaction which is occurring during regeneration, an energy savings for the heat of reaction is also realized.

In addition to the sensible heat and heat of reaction, a major contributor to the regenerator heat duty in an MEA process is the heat of vaporization to generate steam to carry the CO_2 overhead in the stripper. A reflux ratio of 2.0 moles of water per mole of CO_2 is common [21]. The energy required to generate this amount of steam is an additional 18.9 kcal/mol of CO_2 evolved. Since the regeneration of the aqueous ammonia solutions was conducted without this steam requirement, an additional energy savings is expected. Table 1 shows the relative contribution of these energy requirements, comparing the current MEA process to the proposed aqueous ammonia process.

Table 1. Regeneration Heat Required. Comparison of a 14% Aqueous Ammonia Solution to Current MEA Technology

Process	ΔH_{rx} (kcal/mol)	Sensible Heat[*] (kcal/mol)	Heat of vaporization (kcal/mol)	Total (kcal/mol)	% Reduction From MEA process
MEA	20.0	79.4	18.9	118.3	0
$2NH_4HCO_3(aq) = (NH_4)_2CO_3(aq) + CO_2 + H_2O$	6.4	36.0	0	42.4	64
$NH_4HCO_3(aq) = NH_3(aq) + H_2O + CO_2$	15.3	36.0	0	51.3	57
$(NH_4)_2CO_3(aq) = 2NH_3(aq) + H_2O + CO_2$	24.1	36.0	0	60.1	49

CONCLUSIONS

Rates of CO_2 absorption in aqueous ammonia solution were measured. The experiments took place in a semi-continuous reactor at controlled temperatures of 60 ^{0}F, 80 ^{0}F, and 100 ^{0}F. Simulated flue gas at 15%vol CO_2 and 85%vol N_2 was fed into the aqueous ammonia solution through a sintered metal gas sparger to promote gas-liquid mixing. The liquid absorbent was not circulated. The rates of CO_2 absorption were measured at 7%, 14%, and 21% ammonia concentration by weight.

Thermal regeneration of standard solutions revealed that regeneration of up to 60% of the carbon in a bicarbonate solution may be regenerated. Cycling tests results demonstrated that a 64% reduction in regeneration energy is possible due to the higher loading capacity of an aqueous ammonia solution, the lower heat of reaction, and the lower heat of vaporization when compared to standard MEA solutions

Future research work will investigate removals of sulfur dioxide and nitric oxides in the ammonia solution. Work will also be conducted to determine the mechanism of the reactions involved in the absorption/regeneration reactions, in preparation for optimization of the efficiency of the Aqua-Ammonia process for CO_2 separation.

DISCLAIMER

Reference in this report to any specific commercial process, product, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

REFERENCES:

[1] Herzog, H. Editor, The Capture, Utilization and Disposal of Carbon Dioxide from Fossil Fuel-Fired Power Plants. DOE/ER-30194, 1993; Vol. 1.

[2] Herzog, H., E. Drake, and E. Adams, ed. <u>CO2 Capture, Reuse, and Storage Technologies for Mitigating Global Climate Change, A White Paper Final Report.</u> January, 1997. DOE Order No. DE-AF22-96PC01257.

[3] Chakma, A. and P. Tontiwachwuthikul. <u>Designer Solvents for Energy Efficient CO2 Separation.</u> <u>Greenhouse Gas Control Technologies,</u> Riemer, P., B. Eliasson and A. Wokaun, editors, 1999 Elsevier Science Ltd.

[4] NPCC. <u>Study on CO2 Sequestration by Spray Concentrated Aqueous NH3 and Production of Modified NH4HCO3 Fertilizer - a Proposal for US-China joint research.</u> State Engineering Technology Research Center of Combustion of Power Plants (NPCC), China. May, 2000.

[5] Kirk-Othmer, Editor, <u>Encyclopedia of Chemical Technology</u>, 2nd Ed., Vol. 2, 1963.

[6] Shale, C.C., D.G. Simpson, and P.S. Lewis. <u>Removal of Sulfur and Nitrogen Oxides from Stack Gases by Ammonia</u>. Chem. Eng. Prog. Symp. Ser. 1971; 67: 52-58.

[7] Kohl, A and R. Nielsen, <u>Gas Purification</u>, 5th edition, Gulf Publishing Co.

[8] Walsh, M. A. Jr. <u>New Marsulex Technology Significantly Cuts Power Generation Costs</u>. Marsulex Environmental Technologies, LLC, Corporate Publication. 2000.

[9] Lunt, R. R., Arthur D. Little, Inc.; and J. D. Cunic, ExxonMobil Research and Engineering Company. <u>Profiles in Flue Gas Desulfurization</u>. Center for Waste Reduction Technologies (CWRT), published by AIChE. 2000.

[10] Schulte, W. Flue <u>Gas Cleaning with Ammonia Reduces SO2 and NOx Emissions.</u> Proc. Annu. Int. Pittsburgh Coal Conference, 1996, 13, (2), 1474 - 1479.

[11] Kasper, J. M., C. A. Clausen III, and C. D. Cooper, <u>Control of Nitrogen Oxide Emissions by Hydrogen Peroxide-Enhanced Gas-Phase Oxidation of Nitric Oxide</u>. J. AWMA, Vol.46, pp127-133. Feb. 1996.

[12] Cooper, Hal B. H. <u>Removal and Recovery of Nitrogen Oxides and Sulfur Dioxide from Gaseous Mixtures Containing Them</u>. U. S. Patent 4426364, Jan. 17, 1984.

[13] Senjo, T. And M. Kobayashi, <u>Process for Removing Sulfur Oxides and/or Nitrogen Oxides from Waste Gas</u>. U. S. Patent: 4035470, July 12, 1977.

[14] Mimura, T., et al. <u>Process for Removing Carbon Dioxide and Nitrogen Oxides from Combustion Gases</u>. U. S. Patent: 5648053. July 15, 1997.

[15] Bai, H. and A.C. Yeh, <u>Removal of CO2 Greenhouse Gas by Ammonia Scrubbing.</u> Ind. Eng. Chem. Res., Vol. 36, No. 6, 1997.

[16] Yeh, A.C. and H. Bai, <u>Comparison of Ammonia and Monoethanolamine Solvents to Reduce CO2 Greenhouse Gas Emissions</u>. The Science of Total Environment, pp 121-133, 228, 1999.

[17] J. T., <u>Personal Communication on research data of CO2 capture by ammonia solution.</u> NETL/DOE, 2000.

[18] Wolsky, A.M., E.J. Daniels, and B.J. Jody. <u>CO_2 Capture from the Flue Gas of Conventional Fossil Fuel-Fired Power Plants</u>. Environ. Prog. pp 214-219, 13, 1994.

[19] Lee, S. and Tsui, Y., <u>Succeed at Gas/Liquid Contacting,</u> Chemical Engineering Progress, July 1999.

[20] Goff, G.S. and G.T. Rochelle<u>. Oxidative Degradation of Aqueous Monoethanolamine in CO_2 Capture,</u> AICHE Annual Meeting, 2002.

[21] Niswander, R.H., Edwards, D.J.; DuPart, M.S. and J.P. Tse. <u>A More Energy Efficient Product for Carbon Dioxide Separation</u>, Separation Science and Technology, 1993, 28(1-3), pp 565-78.
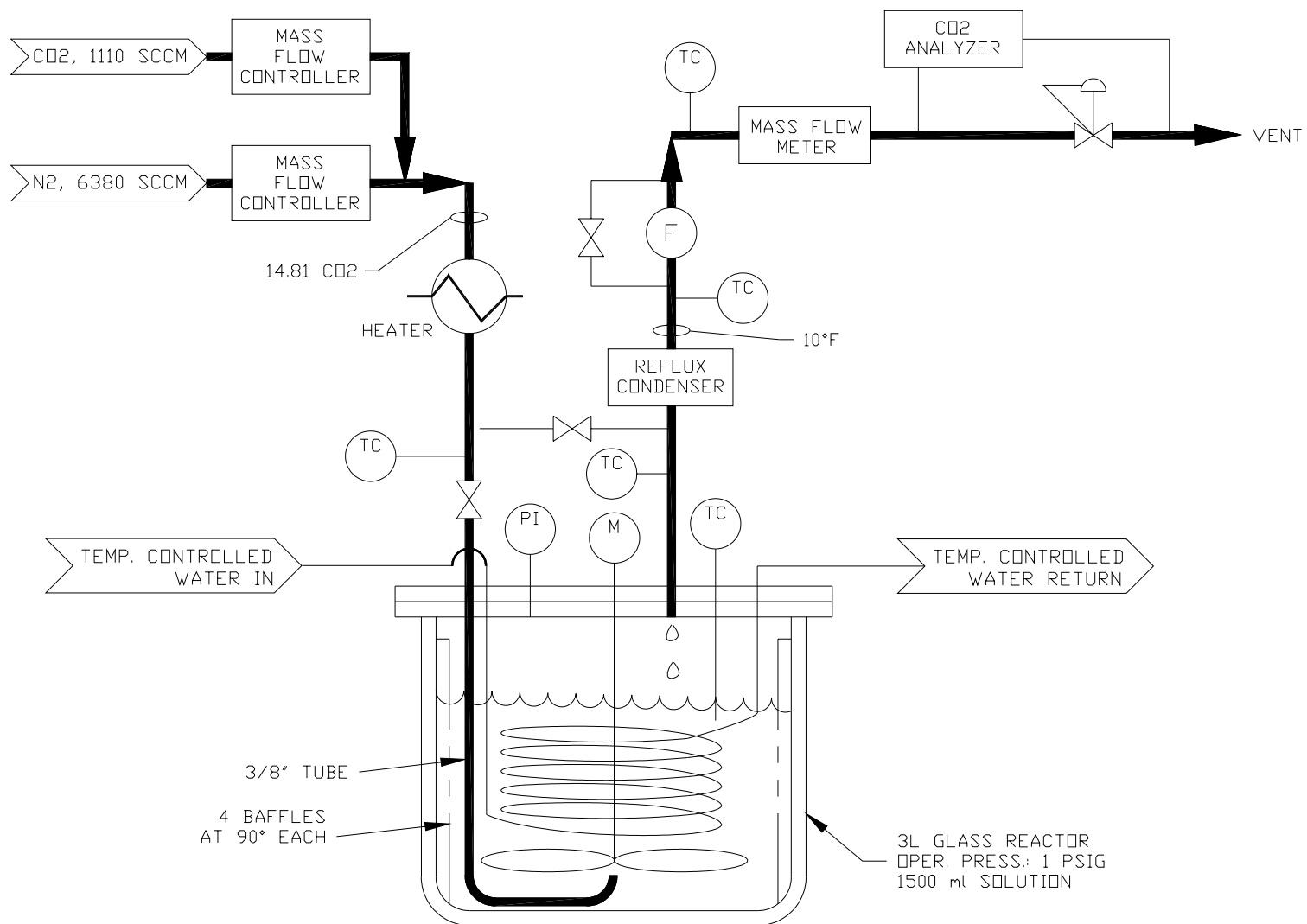
Figure 1.   Aqua Ammonia Semi-Continuous Reactor
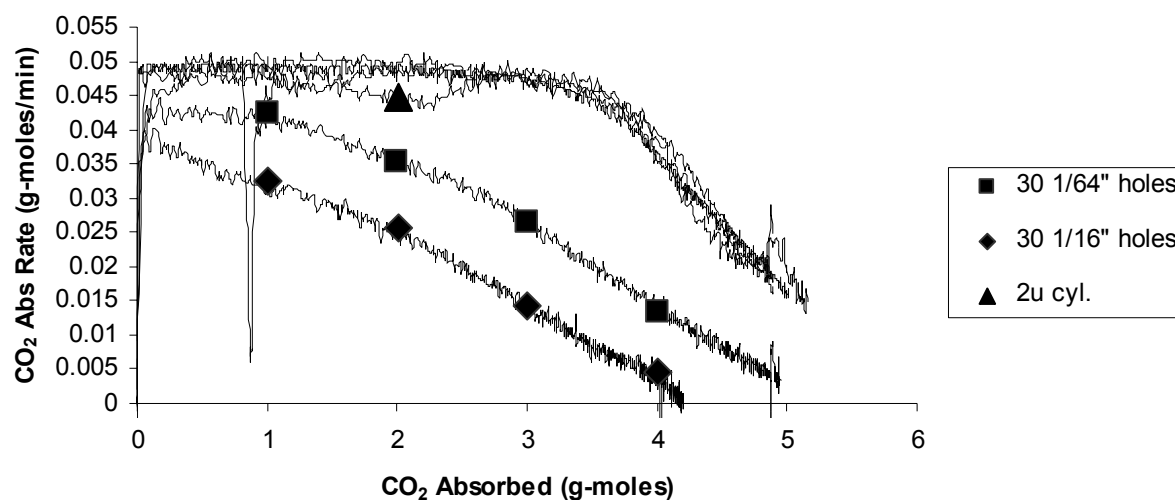
Figure 2.   Effect of Sparger Types (CO$_2$ absorbed)
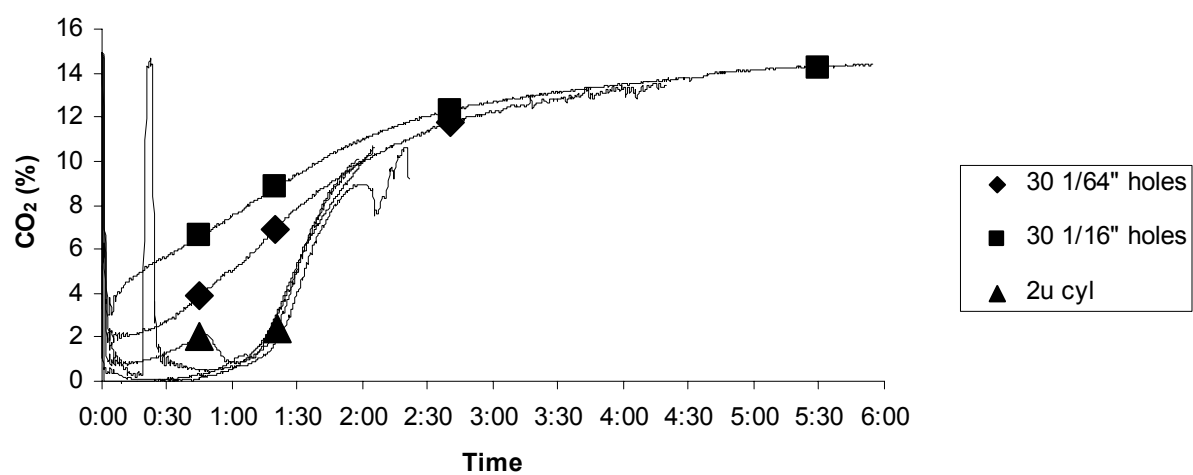
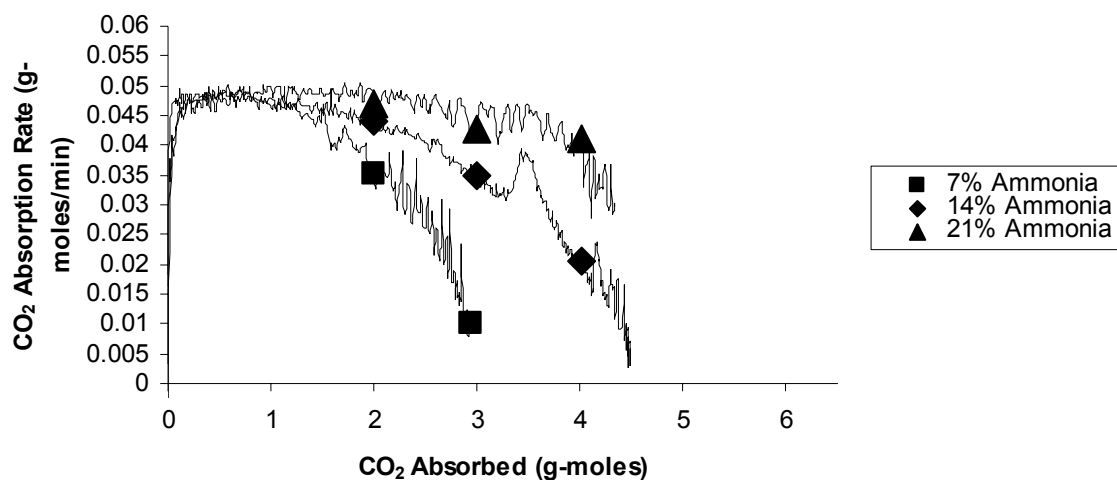**Figure 3. Effect of Sparger Types (CO$_2$ % vs. time)**

15
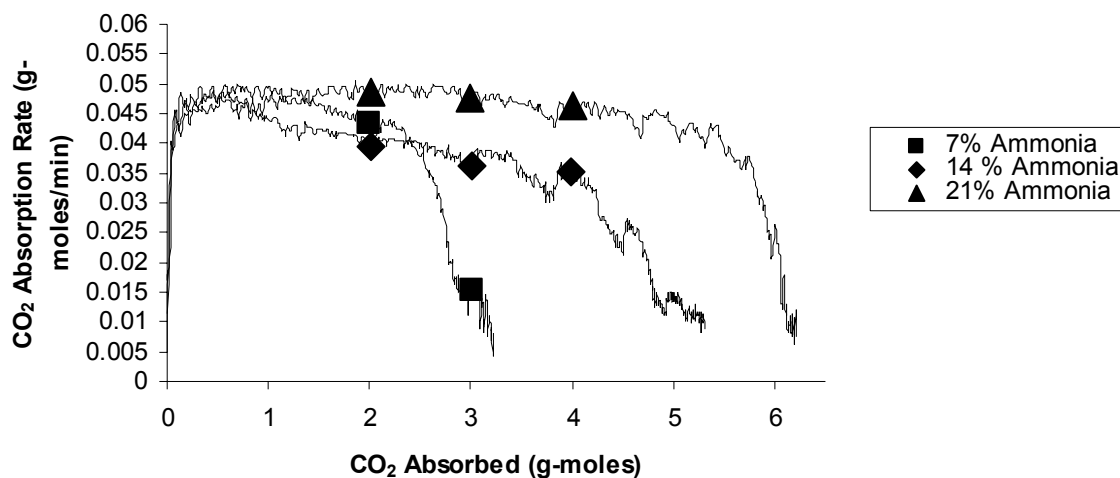
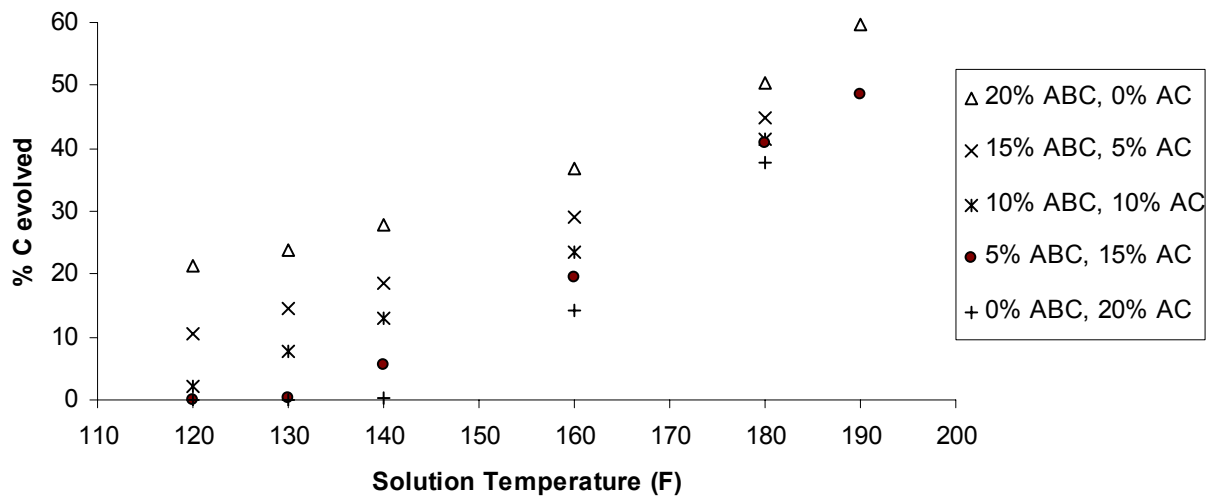**Fig. 4. CO_2 Absorption Rate at 60°F.**
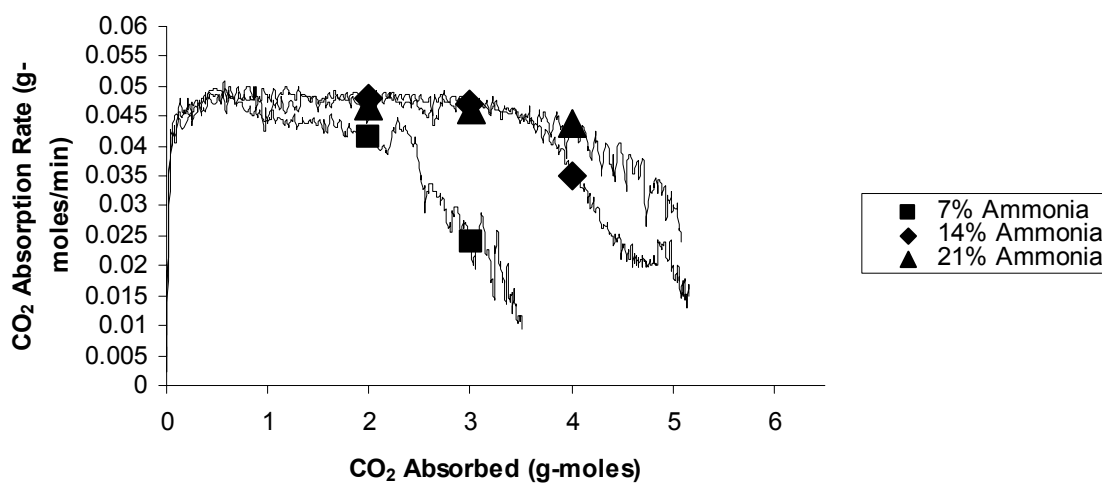
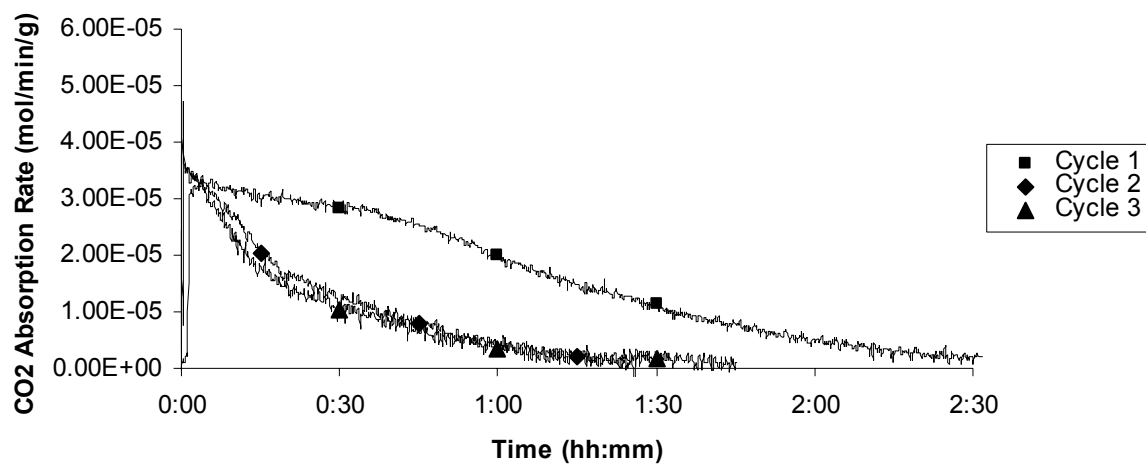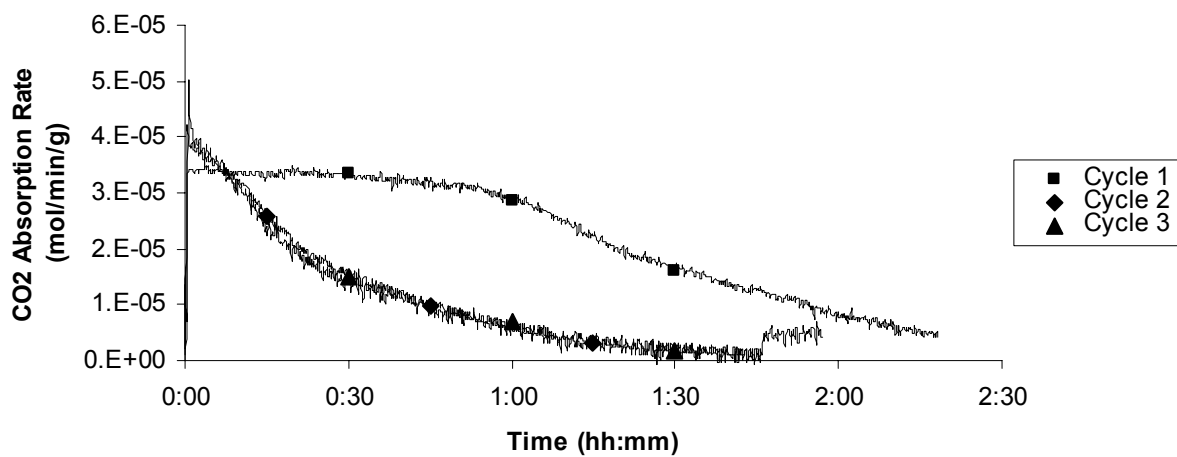**Fig. 5. CO_2 Absorption Rate at 80°F.**
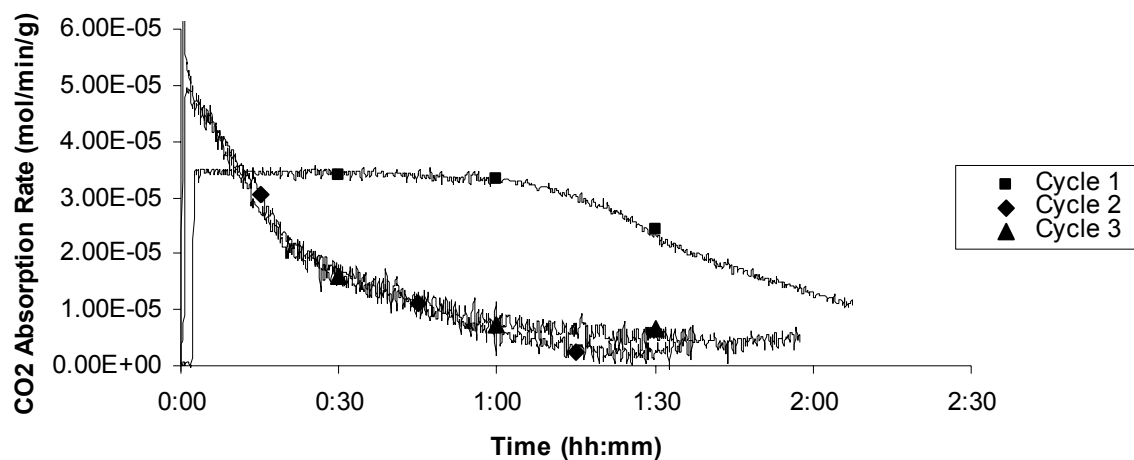
Fig. 6. CO_2 Absorption Rate at 100^oF.
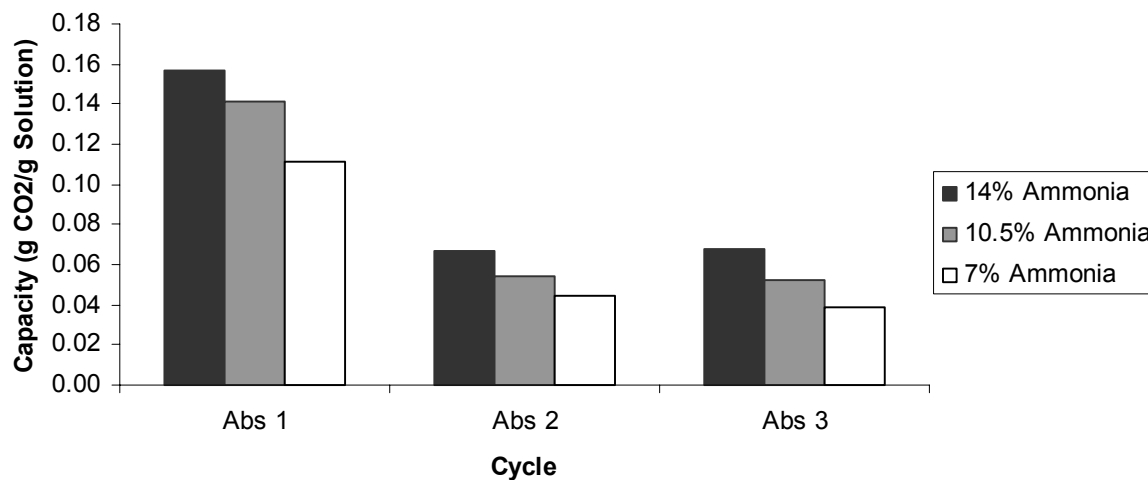

Figure 7. Regeneration Test Summary

Figure 8.   7% NH$_3$ CO$_2$ Absorption Rate

Figure 9.
10.5% NH3 CO$_2$ Absorption Rate

Figure 10. 14% NH3 CO$_2$ Absorption Rate

Figure 11. Effect of Cycling on CO$_2$ Absorption Capacity